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OXIDATION-SORPTION METHOD OF MANGANESE REMOVAL FROM UNDERGROUND WATER

Abstract. The Paper presents the effects of the purification of the underground waters with high manganese contents and oxidizability. The Authors suggest innovative oxidation–based manganese removal technology with continuous introduction of reaction catalytic agent.

Keywords: manganese removal, sorbent modification, underground waters

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ОКИСЛИТЕЛЬНО-СОРБЦИОННЫЙ МЕТОД УДАЛЕНИЯ МАРГАНЦА ИЗ ПОДЗЕМНЫХ ВОД

Аннотация. Представлены результаты очистки подземных вод с высоким содержанием марганца и повышенной окисляемости. Предложена новая технология деманганации на основе окисления с постоянным вводом катализатора реакции.

Ключевые слова: деманганация, модификация загрузки, подземные воды.

Removal of iron and manganese form underground waters with high manganese contents and oxidizability in noncentralised water supply environment can be realized by means of development, research and adoption of up-to-date high-performance water treatment technology employing reliable small water purification units. Hence, the following trends are considered urgent nowadays: development and application of supplementary techniques in order to enhance iron and manganese removal processes; search for optimal doses and reagent combinations; research of modern catalytic material properties.

Soluble manganese contents in oxygen-deficient underground and surface waters of the Sverdlovsk region reach 5 ppm. Russian sanitary norms restrict maximum admissible manganese contents in domestic water up to 0.1 ppm, while in some European countries this value is allowed to be lower than 0.05 ppm. The excess of manganese contents deteriorates organoleptic properties of water. Manganese being higher than 0.1 ppm causes spots on sanitary wares and film on pipelines. The latter is peeled off in the form of dark sediment [1].

Manganese in underground waters is presented as ion Mn^{2+}, salts of which are soluble. To remove manganese from water one should transfer it to insoluble state by oxidation Mn^{2+} to Mn^{3+} and Mn^{4+}. Oxidized manganese compounds are cleaved with the formation of practically insoluble hydroxides $Mn(OH)_3$ and $Mn(OH)_4$. The latter when precipitated through crushed diatomaceous rock (granular sorbent) exhibits catalytic properties, i. e. accelerates Mn^{2+} oxidation process by dissolved oxygen.

Manganese oxidizes within the range of high pH values and oxidation-reduction potentials. Optimum oxidation value for manganese bicarbonate oxidation is pH=10 compared to pH=7, which is optimum value for ferrous bicarbonate to be oxidized by air. The lower pH values can only be kept by applying stronger oxidizing agents (chlorine, ozone, etc.) with their high excess in the reaction [2].

Both iron and manganese are found in underground waters but it is iron that is removed from water at deferrization plants in operation utilizing aeration followed by filtration. Due to strong oxidizing agents, manganese ox-

idizes and sorbs only after iron since the latter is an easily oxidizable element. Therefore, joined purification of iron and manganese on the same stage at filter plants is feasible provided their concentration equals minimum values up to 2–5 ppm and strong oxidizing agents are employed.

Sanitary norms [3] on manganese removal directly in deferrization without adding reagents are outdated and fail to meet present requirements of the processes described. Application of various schemes to purify water from manganese or iron or both depends on contaminant concentration, plant capacity and local conditions.

Underground waters of the Sverdlovsk region are mainly polluted by manganese, although it is non-typical in some cases when the contents of manganese exceed those of iron.

The research of manganese removal in the city Verkhnaya Pyshma conducted by the Department of Water Industry and Water Technology in Ural Federal University proved the concentration of manganese to be 4.5 ppm, ferrum — 0.6 ppm, silicon — 17 ppm, oxidizability — 5.5 mgO_2/l and pH = 6.8. According to the suggested reagent purification scheme, corresponding reagents were added into water, then it was immediately filtered through light granular sorbent at 10–12 m/hr. Preliminary research showed that mixing such water with oxygen or chlorine combined with alkalization regardless of reagent dose did not lead to manganese retention.

Then, tests were carried out to oxidize manganese with potassium permanganate followed by filtration and the results are presented in Fig. 1. Introduction of even low doses of potassium permanganate reduced the concentration of manganese in filtrate up to 1.5–2 ppm. However, the purification efficiency wasn't affected by the increase of the dose. This results from permanganate being used for oxidation of organic matters. Once the concentration of potassium permanganate is higher than 20 ppm, sharp increase of manganese contents in filtrate occurs because of permanganate migration to filtrate. Given contact time of high dose of reagent with water is increased in the following filtration, the water of drinking quality is likely to obtain by means of such process. This proves the occurrence of additional processing operation and the necessity to mount the reactor prior to fast filter.

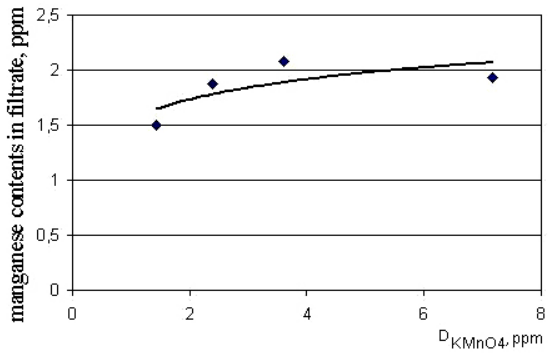

Fig. 1. Dependence of manganese concentration on potassium permanganate dose (pH = 6.8) in filtrate

For manganese to oxidize effectively, the value pH of water to be purified should be 8.0–8.5 [2]. Previous experiment was repeated but water was additionally alkalified with caustic soda with pH up to 8.5. The results are presented in Fig. 2.

As it shown in Fig. 2 the increase of potassium permanganate dose results in the decrease of manganese contents in filtrate. But the dependence is not linear; the higher the dose, the slower the growth of the purification efficiency.

While filtering the water mixed with potassium permanganate, the sorbent was modified: its granules were covered with the layer of manganese hydroxide performing several functions simultaneously — being an oxidation reaction catalytic agent, oxidizing manganese and sorbing organic compounds. Water was purified in such modified sorbent; meanwhile oxidizing agent (sodium hypochlorite) and alkalifying agent (cauistic soda) were added into water. Fig. 3 shows the results of the experiment.

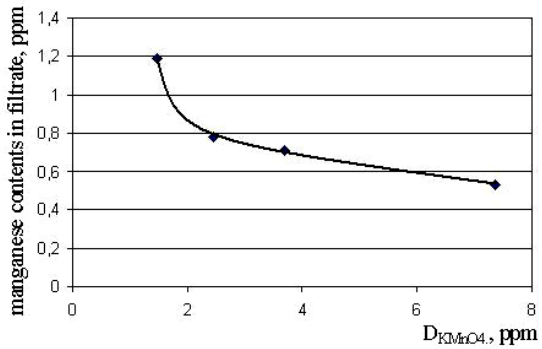

Fig. 2. Dependence of manganese concentration on potassium permanganate dose (pH = 8.5) in filtrate

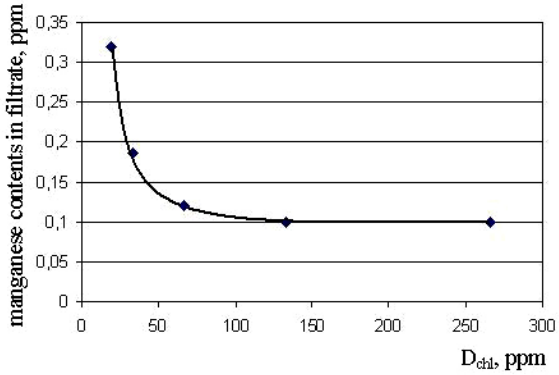

Fig. 3. Dependence of manganese concentration on available chlorine dose (pH = 8.5) in filtrate

On the graph one can see that manganese is removed to drinking sanitary norms when chlorine dose is higher than 100 ppm in modified sorbent. Residual chlorine accounts for 80 ppm necessitating additional processing operation on its removal. In addition, organic matters and silicon compounds causing progressive decrease of purification efficiency gradually contaminate catalytic layer (the layer of manganese hydroxide on granule surface).

To avoid shortcomings of the above-listed processes, the manganese removal technology based on the application of granular sorbent with renovating catalytic layer was developed. The technology implies adding into water alkalifying and oxidizing (sodium hypochlorite) agents. Besides potassium permanganate constantly added to water accounts for 2–5 ppm. Potassium permanganate reacts instantly with manganese and organic matters creating insoluble suspension of manganese hydroxide — catalytic agent of manganese oxidation reaction. Sorbent is constantly modified by new doses of catalytic agent. In such sorbent, the contaminated catalytic agent tends to be covered with a new film of manganese hydroxide enabling oxidizing soluble manganese even with low amount of available chlorine. The sorbent should be regenerated every 6 hours by backwash as the growing catalytic layer is squeezed out to filtrate.

On the basis of this technology the manganese removal plant with the capacity of 300 m^3 per day was created in Verkhnaya Pyshma. Potassium permanganate available dose accounted for 3 ppm, chlorine dose was 5 ppm. Manganese concentration after purification was less than 0.005 ppm. The operation of the plant for a year has proved the reliability and efficiency of the suggested technology.

References

1. *Manual on drinking water quality control*. Vol.1. Geneva, WHO, 1994. 257 p.

2. Kulakov V. V., Soshnikov E. V., Chaikovskii G. P. *Obezzhelezivanie i demanganatsiia podzemnykh vod* [Iron and manganese removal]. Khabarovsk, DGUPS Publ., 1998. 100 p. (In Russ.).

3. *SNiP 2.04.02–84*. Vodosnabzhenie. Naruzhnye seti i sooruzheniia* [Water Supply. Public Utilities]. Moscow, GP CPP, 1996. 128 p. (In Russ.).